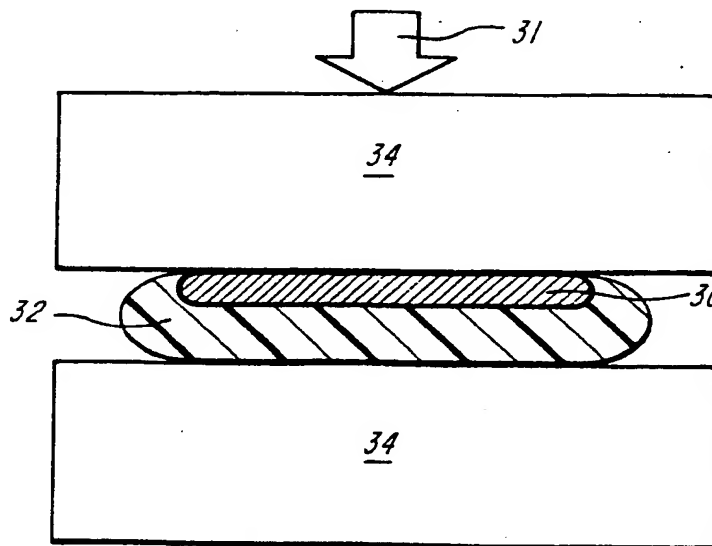




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B05D 5/12, 3/12	A1	(11) International Publication Number: WO 92/13649 (43) International Publication Date: 20 August 1992 (20.08.92)
(21) International Application Number: PCT/US92/01118 (22) International Filing Date: 10 February 1992 (10.02.92) (30) Priority data: 652,528 8 February 1991 (08.02.91) US (71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). (72) Inventors: GAO, Wei ; 104 Albion Street, Somerville, MA 02144 (US). VANDER SANDE, John, B. ; 5 High Road, Newbury, MA 01951 (US). (74) Agent: PASTERNAK, Sam; Choate, Hall & Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>

(54) Title: A METHOD FOR SYNTHESIS OF HIGH T_c SUPERCONDUCTING MATERIALS BY OXIDATION AND PRESS COATING OF METALLIC PRECURSOR ALLOYS

**(57) Abstract**

A superconductor oxide composite is prepared using a press coating technique. The coated layers on various substrates exhibit good adhesion, textured microstructure, and improved J_c .

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MI	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

**A METHOD FOR SYNTHESIS OF HIGH T_c SUPERCONDUCTING MATERIALS
BY OXIDATION AND PRESS COATING OF METALLIC PRECURSOR ALLOYS**

The United States Government retains rights to this
5 invention based upon funding by the Department of Energy under
Contract DE-FG02-85ER-45179.

Background of the Invention

This invention relates to press coating and oxidation of
10 metallic precursor alloy synthesis methods for high T_c
superconducting materials.

Bulk, high T_c superconducting oxides suitable for power
transmission applications have been synthesized with a number
of processing techniques. These techniques include high
15 temperature oxidation of metallic precursor alloys containing
metallic constituents of desired superconducting oxides. Such
metallic precursors can be made by any metal forming technique
depending upon the required superconductor shape including
melt spinning, planar flow casting, melt dipping and melt
20 writing. Metallic precursors can contain metals stable
through oxidation processing including noble metals such as
silver to produce superconducting oxide/metal microcomposites
with combined good mechanical and superconducting electrical
properties.

25

Summary of the Invention

According to one aspect of the invention, high T_c oxide
superconductor composites are synthesized by pressure coating
a substrate with oxidized metallic precursor alloy.

30 As an example of the invention, a Bi-Pb-Sr-Ca-Cu-O
superconductor composite is synthesized by pressure coating a
substrate with an oxidized Bi-Pb-Sr-Ca-Cu/noble metal
precursor alloy to produce the Bi-Pb-Sr-Ca-Cu-O/noble metal
superconductor composite. Other superconducting systems

including Yb-Ba-Cu-O, Y-Ba-Cu-O, and Tl-Ba-Ca-Cu-O can be processed with the press coating method.

In some embodiments, the metallic precursor alloy can be prepared using any metals processing technique including melt spinning, melt dipping, and melt writing. The oxidized metallic precursor alloy can be pressed or rolled onto the substrate at temperatures between 25°C-800°C and pressures between 1 and 20 MPa. Substrate materials can be pure metals such as Ag, Au, Pt, Pd, Cu or Ni; stainless steel and nickel alloys; composites including Ag sheets on stainless steel and Ag sheets on Fe, Co, Cu, and Ni alloys, and metal/ceramic composites and ceramics. The Bi-Pb-Sr-Ca-Cu metallic precursor can contain surplus Ca or Cu.

In other embodiments, multiple layers whose thickness and width are controlled by adjusting processing conditions, can be applied to a substrate. Superconducting properties can be optimized by design of suitable heat treatments and multiple press/anneal sequence repetition. Selected mechanical deformation and atmospheric conditions can be combined to enhance superconductor texturing.

In other embodiments, the method can be used to produce high T_c superconductor coatings in a variety of geometries including large or small areas with flat, smooth surfaces and uniform thickness, long wires, and ribbons of selected thickness. Protective coatings can be pressed or rolled onto superconductor coatings using this technique.

Press coating can be used in combination with other superconductor preparation techniques including melt dipping and melt writing methods to further enhance superconducting and mechanical properties. Press coating can be used to join superconductors or fabricate superconductor/normal metal joints. Press coating can also be used in combination with superconducting oxides prepared by other fabrication techniques including powder processing of the individual metal oxides and pyrolysis of metal-organo precursors.

Compared with conventional ceramic processes or the simple metallic precursor oxidation method, the present method offers several advantages. The pressing or rolling treatment produces a dense superconductor coating. The resulting composite has good mechanical properties based on substrate strength and toughness combined with good adhesion between coating and substrate. Combined mechanical deformation and controlled atmosphere annealing produces textured microstructures, characterized by increased critical current density. This method offers considerable flexibility in fabrication of varied geometry composites including wire, narrow or wide ribbon, and small or large area coatings. Coating thickness is uniform (typically 5-200 μm), and can be accurately controlled by the pressing or rolling process.

The product of the oxidation and press coating method is typified by having a textured microstructure with platelike grains of superconductor phase aligned parallel to the substrate plane. The superconductor composite contains no gap between the coating and the substrate.

Brief Description of the Drawing

Fig. 1 is a schematic illustration of the press coating process;

Fig. 2 is a schematic illustration of the press coating of a multi-layered superconductor composite;

Fig. 3 is an SEM backscattered electron (BSE) micrograph from a polished, longitudinal cross-section of multi-layered $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{21}$ ribbon pressed on a Ag substrate after suitable oxidation and annealing;

Fig. 4 is an SEM backscattered electron (BSE) micrograph from a polished longitudinal cross-section of a multi-layered $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{21}$ ribbon pressed on a Au substrate after suitable oxidation and annealing;

Fig. 5 is an SEM (BSE) cross-section micrograph for an oxidized $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{21}$ alloy press-coated onto a Ag substrate after suitable oxidation and annealing;

Fig. 6 is an SEM (BSE) cross-section micrograph for a $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{11}$ alloy press-coated onto a Ag substrate after suitable oxidation and annealing;

Fig. 7 is an SEM (BSE) micrograph for a $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{36}$ alloy pressed on a Ag substrate after suitable annealing; and

Fig. 8 is an SEM (BSE) micrograph for $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{11}$ alloy pressed on a Ag substrate after suitable oxidation and repeated pressing and annealing.

10

Description of the Preferred Embodiment

In a preferred embodiment, Bi-Pb-Sr-Ca-Cu-O/Ag microcomposites were fabricated on Ag, Au, Cu, Pt, Pd, Ni and silver sheet covered stainless steel substrates.

15 Precursor alloy ribbons were produced by vacuum melting and melt spinning rapid solidification of alloys with nominal compositions (atomic proportions) $1.4\text{Bi}-0.6\text{Pb}-2\text{Sr}-3\text{Ca}-4\text{Cu}$ with 5, 11, 21 and 36Ag, corresponding to 35-80 wt.%Ag. Surplus Ca and Cu in the alloys is necessary for obtaining a well
20 developed "2223" superconducting phase. Ribbon thickness and width ranged typically from 50-70 μm and 2 to 3 mm respectively. Ribbons were fully oxidized at 500-600°C in 100% O_2 for 40h and annealed at 820°C in 5% O_2 + 95%Ar for 8h prior to press coating. Pure Ag sheets ($\geq 99.9\%$ Ag) 0.025-
25 0.25mm thick, Au, Pt, Pd, Ni, Cu sheets 0.051 mm thick, and stainless steel plates (≈ 0.3 mm) covered by 0.025 mm thick Ag sheet were used as substrates. Metallic substrates were used as received without further polishing. Substrates were cleaned with dry methanol and distilled water.

30 Press coating was conducted in a PR-22 Pneumatic Mounting Press under 2-10MPa pressure at 160°C. Substrates of approximately 3x10mm dimensions and ribbon were positioned between two steel dies. Fig. 1 shows one piece of ribbon 30 being pressed as indicated by arrow 31 on substrate 32 by dies.
35 34. Alternately, substrates 10 and five layers of ribbon 12,

14, 15, 16, and 18 were positioned between dies 20 with or without lubricating teflon films 22 as shown in Fig. 2. Pressure was applied slowly in the direction given by arrow 24, held for at least 4 minutes, and released.

5 Press-coated layers were flat, with smooth, shiny surfaces and uniform thicknesses. The degree of adhesion between coating and substrates depends upon substrate properties, applied pressure and processing temperature. Substrate/coating adhesion has been qualitatively classified
10 by visual inspection after cooling, heat treatment and slow bending to approximately 20 degree angles.

Coatings on Ag substrates exhibited the best adhesion, followed by those on Au, Cu and Pd substrates. Coating adhesion on Ag and Au was satisfactory, without spalling or
15 delamination even after subsequent annealing, cooling and bending to 20 degrees. Coatings on Pt, Ni and 304 stainless steel were not adherent. Coatings on Pt, Ni or stainless steels were made adherent by pressing two substrate sheets with teflon films on both sides of the coatings, as shown in
20 Fig. 2.

Pressing caused coating and substrate deformation. The extent of deformation depended on applied pressure, coating and substrate materials, processing temperature and lubrication. A thickness reduction ratio R was used to
25 describe the deformation, as

$$R = t_2/t_1$$

where t_1 and t_2 are the coating thickness before and after pressing, respectively. Table I shows thickness reduction ratio R , applied pressure, coating and substrate materials,
30 and adhesion behavior of coated layers.

As shown in Table I, ratios R vary from 0.30 to 0.45 for $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{Ag}_{21}$ coatings on different substrates subject to identical pressing conditions of 8 MPa without lubrication. Deformation decreased in order for Au, Ag, Cu, Pd, Pt and Ni
35 substrates consistent with the different hardness, ductility

and contact friction characteristic of these metals. Lubricant teflon films reduced contact friction and increased deformation by 30-40%, and made behavior of different substrates more uniform.

- 5 Adhesion and deformation of coatings also depended on applied pressure. A ≥ 4 MPa pressure was needed for good coating adhesion on Ag, while pressure ≥ 10 MPa caused large deformation and sample edge cracking. Coating material composition did not affect the deformation ratio
10 significantly. Coatings with different Ag concentrations exhibited similar thickness after pressing, as shown in Table I.

- Press-coated specimens required a second anneal to ensure good superconducting properties. Such anneals removed
15 microcracks created by press/deformation processes which interrupt superconducting grain continuity and adversely affect superconducting properties. Anneals were conducted in 5%O₂+95%Ar atmospheres. Deformation processing and annealing were combined to optimize superconducting properties.
20 Resulting superconducting onset temperature, T_{on} , zero resistance temperature, $T_{R=0}$, and critical current density, J_c , at 77K in zero field are listed in Table II, together with sample pressing and annealing conditions.

- T_c and J_c were measured using a standard four-point probe
25 technique. In $J_c(77)$ measurements, a criterion of 1 μ V/cm was used to define the critical current I_c and the entire coating cross section was used to calculate the critical current density $J_c(77)$. Special attention was given to current passing through the Ag substrate since Ag is an excellent
30 electrical conductor. At 77K, a pure Ag substrate showed a linear plot of voltage versus current at a scale of 1mA, with a slope of order 0.1-1 μ V/mA, while a superconducting coating on a Ag substrate did not show any voltage until the current reached I_c (approximately 1A), when a sharp transition

Table I Deformation Ratio and Pressed Coating Quality

Coating Material	Substrate & Lubricant	Applied Pressure (MPa)	Deformation Ratio $R(=t_2/t_1)^{11}$	Surface Quality & Adhesion ¹²
Bi _{1.4} Pb _{0.8} Sr ₂ Ca ₃ Cu ₄ Ag ₂₁ 600C/48h+820/8h	Ag/NL ¹³	8	0.35	adhesion good smooth surface
	Au/NL	8	0.30	adhesion good smooth surface
	Cu/NL	8	0.36	adhesion fair smooth surface
	Pd/NL	8	0.38	adhesion fair smooth surface
	Pt/NL	8	0.42	no adhesion
	Ni/NL	8	0.45	no adhesion
As above	Ag/TF ¹⁴	8	0.24	adhesion good smooth surface
	Cu/TF	8	0.25	edge cracking
	Ni/TF	8	0.27	smooth surface
As above	Ag/NL	2	0.80	barely adhered
	Ag/NL	4	0.70	adhesion fair
	Ag/NL	6	0.40	smooth surface
	Ag/NL	10	0.32	adhesion good smooth surface edge cracking
Bi _{1.4} Pt _{0.8} Sr ₂ Ca ₃ Cu ₄ Ag ₅ 400C/48h+820/8h	Ag/NL	8	0.33	adhesion fair
Bi _{1.4} Pb _{0.8} Sr ₂ Ca ₃ Cu ₄ Ag ₁₁ 600C/48h+820/8h	Ag/NL	8	0.35	surface roughness adhesion fair
Bi _{1.4} Pb _{0.8} Sr ₂ Ca ₃ Cu ₄ Ag ₃₈ 600C/48h+820/8h	Ag/NL	8	0.35	smooth surface adhesion good smooth surface

¹¹ Obtained by pressing the coating with two substrates on both sides; t_1 and t_2 are the coating thickness before and after pressing.

¹² Obtained by pressing the coating to a metal substrate.

¹³ NL indicates pressing without lubrication.

¹⁴ TF indicates pressing with teflon sheets as lubricant.

Table II Pressing, Oxidation and Annealing Conditions With Resultant Superconducting Properties

Alloy	Substrate	Treatment	$T_{on}/T_{R=0}$ K	J_c (77) A/cm ²
Bi _{1.4} Pb _{0.6} Sr ₂ - Ca ₃ Cu ₄ Ag ₂₁	Ag	melt writing, without pressing, 600/40h+820/72h	116/106	500
	Ag	600/40h+820/8h+P ₁ ¹ +820/72h	116/105	800
	Au	same as above	114/102	400
	Pt	same as above	70/-	-
	Pd	same as above	110/75	-
	Cu	same as above	80/72	-
	Ni	same as above	76/71	-
	Ag/S.S. ²	same as above	114/102	450
	Ag	600/40h+820/8h+P ₂ ³ +820/72h	116/107	1200
	Ag	600/40h+820/8h+P ₂ +820/72h+P ₂ + 800/48h	116/107	2000
Bi _{1.4} Pb _{0.6} Sr ₂ - Ca ₃ Cu ₄ Ag ₉	Ag	500/40h+820/8h+P ₁ +830/72h	116/100	500
Bi _{1.4} Pb _{0.6} Sr ₂ - Ca ₃ Cu ₄ Ag ₁₁	Ag	550/40h+820/8h+P ₁ +820/72h	114/104	700
Bi _{1.4} Pb _{0.6} Sr ₂ - Ca ₃ Cu ₄ Ag ₃₆	Ag	600/40h+820/8h+P ₁ +815/72h	116/104	750

¹ P₁ = Pressing with two substrates on both sides at 150-200C, pressure = 8MPa.

² Ag/S.S. = Ag sheets covered stainless steel (304).

³ P₂ = Pressing with two substrates on both sides at 150-200C, with teflon films between dies and substrates, pressure=8MPa.

occurred. Hence, it follows that I_c measurements were not significantly affected by the Ag substrates.

As shown in Table II, the pressed coatings on all the
5 substrates used in the present work exhibited superconductivity after annealing. Those on Ag and Au substrates showed $T_{R=0} \geq 100K$, indicating that a well developed "2223" superconductor phase was formed. The coating on Pd showed $T_{on} = -110K$, but $T_{R=0} = 70-80K$, reflecting co-existence of

"2223" and "2212" superconducting phases. Coatings on Cu and Ni showed superconducting transition temperatures of 70-80K, indicating that the superconducting phase was mainly the "2212" phase. Coatings on Pt exhibited superconducting onset temperatures around 70K, with no zero resistance temperatures. Reactions between coatings and certain of these substrates during annealing affected the formation of the superconducting phases. The "2223" phase did not form after coating reaction with Pt, Cu and Ni substrates. The "2212" superconducting phase, however, survived the reactions, probably because of its greater stability.

Substrate/coating reactions can be avoided by covering substrates with Ag sheets. Coatings pressed on Ag covered stainless steel(304) substrates exhibited $T_{R=0} \geq 100K$ and $J_c(77) = 450A/cm^2$, comparable to results with Ag and Au substrates.

Microstructural observation and microanalysis were performed with a JEOL Superprobe 733 Microanalyzer equipped with Tracor Northern 5500-5600 WDS and EDS systems. Backscattered electron images (BSE) show contrast between phases of differing chemical composition. Figs. 3 and 4 show two BSE micrographs of longitudinal cross sectional microstructure of multilayer ribbons of $Bi_{1.4}Pb_{0.6}Sr_2Ca_3Cu_4Ag_{21}$ pressed on Ag and Au substrates. The ribbons were oxidized at 600°C in 100%O₂ for 40h, then annealed at 820°C in 5%O₂ + 95%Ar for 8h before pressing. Pressing was conducted at 8MPa and both sides of the coating were covered by substrates. Specimens were reannealed at 820°C in 5%O₂ + 95%Ar for 72h. Substrates are marked to indicate Ag or Au, bright areas are Ag, plate-like, light gray grains are "2223" superconducting phase, and the dark grains are non-superconducting oxides.

As shown in Fig. 3, no gap is visible between the coating and Ag substrate, indicating that there is no coating/substrate reaction. Coating adhesion is very good. In Fig. 4, a dark area close to the Au substrate indicates

that some reaction took place at that interface. The affected area was thin (5-10 μ m wide), and did not compromise superconducting properties significantly.

Figs. 5, 6 and 7 are BSE micrographs of
5 Bi_{1.4}Pb_{0.6}Sr₂Ca₃Cu₄Ag₅, Bi_{1.4}Pb_{0.6}Sr₂Ca₃Cu₄Ag₁₁, and
Bi_{1.4}Pb_{0.6}Sr₂Ca₃Cu₄Ag₃₆ coatings on Ag substrates oxidized
sequentially at 500°C, 550°C and 600°C in 100%O₂ for 40h,
annealed at 820°C in 5%O₂ + 95%Ar for 8h, pressed with 8MPa
and both sides covered with Ag, and reannealed at 820°C in
10 5%O₂ + 95%Ar for 72h. The Ag, "2223" superconducting phase,
and non-superconducting phases have contrasts similar to those
in Figs. 3 and 4. The "2223" superconducting phase (plate-
like, gray grains) was well developed in all three specimens
consistent with the T_c and J_c listed in Table II. The
15 microstructure shows apparent texture with Ag and plate-like
"2223" grains aligned parallel to the substrate plane,
especially for the higher Ag content specimens shown in Figs.
6 and 7. Texturing produced by pressing deformation enhanced
J_c.

20 Fig. 8 is a BSE micrograph for a Bi_{1.4}Pb_{0.6}Sr₂Ca₃Cu₄Ag₂₁
coating pressed on a Ag substrate by repeated pressing and
annealing. Processing included oxidation at 600°C for 40h,
annealing at 820°C for 8h, pressing at 8MPa with Ag sheets and
teflon films, annealing at 820°C for 72h, pressing under the
25 same conditions, and reannealing at 800°C for 48h. The "2223"
phase exhibited better developed texture than is visible in
Figs. 3, 4, 5, 6 or 7. The coating was thin (approximately
20 μ m), and J_c(approximately 2000A/cm²) was further improved.

30 What is claimed is:

1. A method for synthesis of oxide superconductor composites comprising:
 - preparing a metallic precursor alloy containing metallic constituents of the oxide superconductor;
 - 5 oxidizing the precursor alloy;
 - press coating the oxidized precursor onto the substrate to produce the oxide superconductor composite; and
 - reannealing the oxide superconductor composite.
2. A method for synthesis of a Bi-Pb-Sr-Ca-Cu-O
10 superconductor composite comprising:
 - preparing a metallic precursor BiPbSrCaCu/noble metal precursor alloy;
 - oxidizing the precursor alloy; and
 - press coating the oxidized precursor onto ^athe substrate
15 to produce the Bi-Pb-Sr-Ca-Cu-O superconductor composite; and
 - reannealing the Bi-Pb-Sr-Ca-Cu-O superconductor composite.
3. The method of claim 2 wherein the precursor contains surplus Ca or Cu.
- 20 4. The method of claim 2 wherein the noble metal is Ag.
5. The method of claim 1 or 2 wherein the precursor alloy is made by any metals processing technique.
6. The method of claim 5 wherein the metals processing technique is a technique selected from the group consisting of
25 melt spinning, melt dipping, and melt writing.
7. The method of claim 1 or 2 wherein said oxidized precursor is pressed or rolled onto the substrate.
8. The method of claim 1 or 2 wherein the oxidized precursor is pressed or rolled on the substrate at
30 temperatures between 25°C and 800°C.
9. The method of claim 1 or 2 wherein the oxidized precursor is pressed onto the substrate at a pressure between 1 and 20MPa.
10. The method of claim 1 or 2 wherein the oxidation of
35 said precursor alloy is partial.

11. The method of claim 1 or 2 wherein the oxidation of the precursor alloy is complete.
12. The method of claim 1 or 2 wherein the substrate is a pure metal.
- 5 13. The method of claim 12 wherein the metal is a metal selected from the group consisting of Ag, Au, Pt, Cu and Ni.
14. The method of claim 1 or 2 wherein the substrate is an alloy.
- 15 15. The method of claim 14 wherein the alloy is an alloy selected from the group consisting of stainless steels and nickel alloys.
16. The method of claim 1 or 2 wherein the substrate is a composite.
- 15 17. The method of claim 16 wherein the composite is a composite selected from the group consisting of Ag/stainless steel, Ag/Fe, Ag/Ni, Ag/Co, Ag/Cu, Ag/Fe alloy, Ag/Ni alloy, Ag/Co alloy, and Ag/Cu alloy composites.
18. The method of claim 1 or 2 wherein the substrate is a metal/ceramic composite.
- 20 19. The method of claim 1 or 2 wherein the substrate is a ceramic.
20. The method of claim 19 where the ceramic is a metal oxide.
- 25 21. The method of claim 1 or 2 wherein the oxidized precursor coatings are applied as multiple layers.
22. The method of claim 21 wherein the thickness and width of layers are controlled by adjusting processing conditions.
- 30 23. The method of claim 1 or 2 wherein the superconductor is subjected to subsequent heat treatment.
24. The method of claim 1 or 2 wherein the superconductor composite is subjected to repeated press/anneal cycles.

25. The method of claim 1 or 2 wherein combined mechanical deformation and selected atmosphere is used to develop texturing.

26. The method of claim 1 or 2 wherein oxidized precursor alloys are applied to substrates of differing geometries.

27. The method of claim 1 or 2 wherein the superconductor composite is further coated with a protective coating.

28. A method for synthesis of oxide superconductor composites comprising:

press coating a superconducting oxide onto the substrate to produce a superconductor oxide composite; and

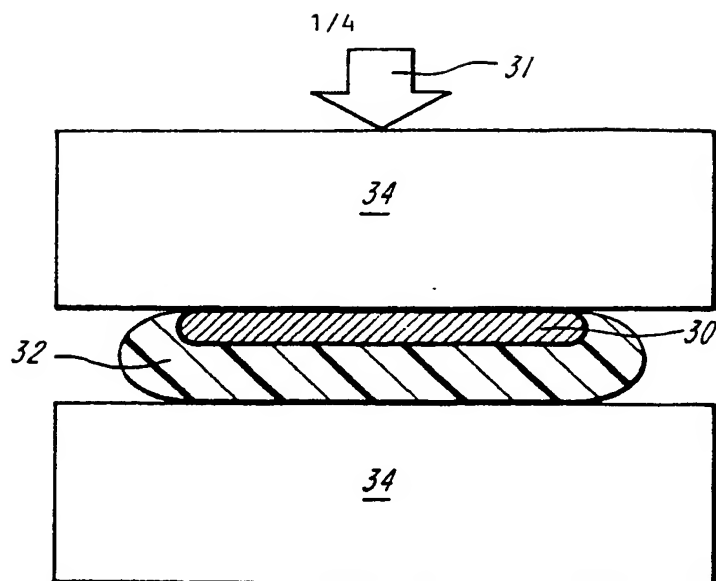
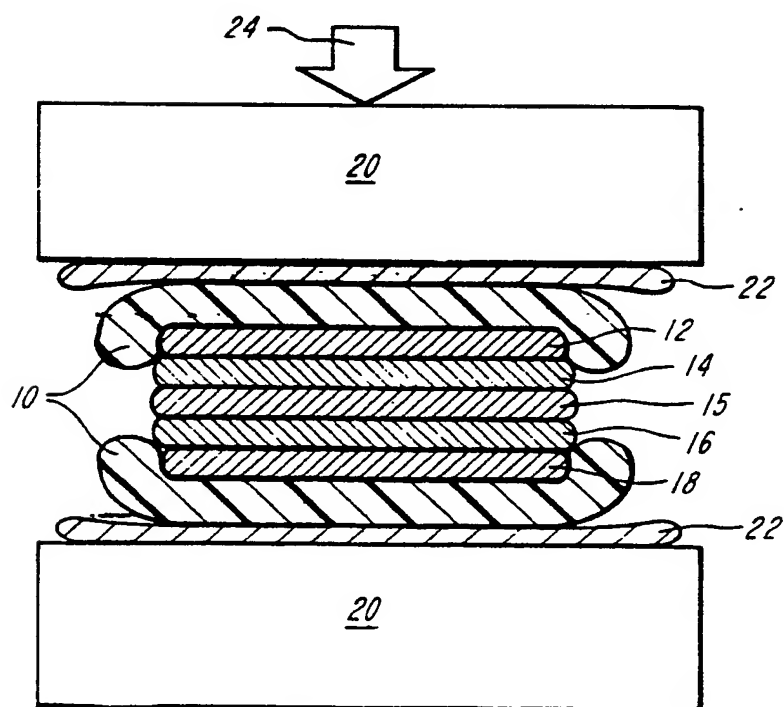
reannealing the oxide superconductor composite.

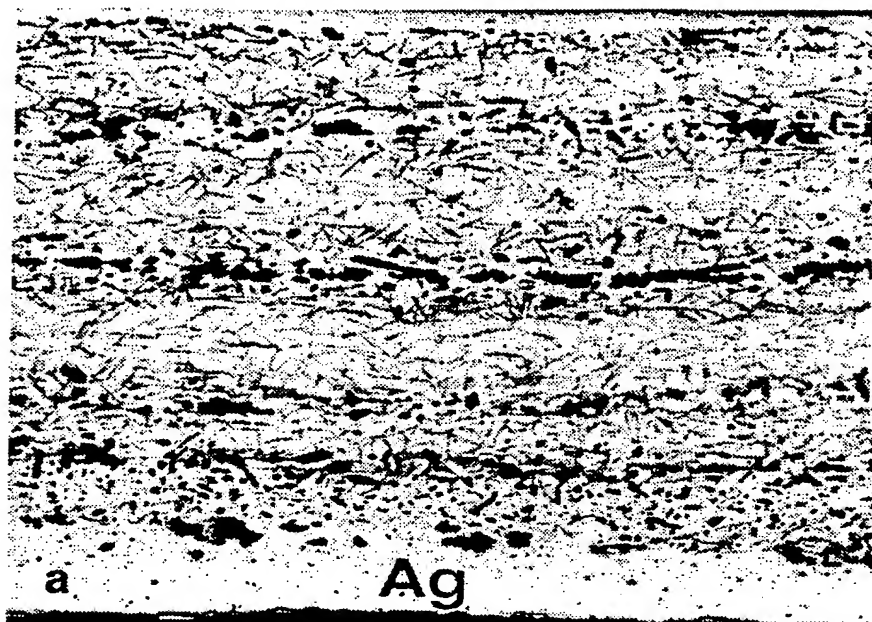
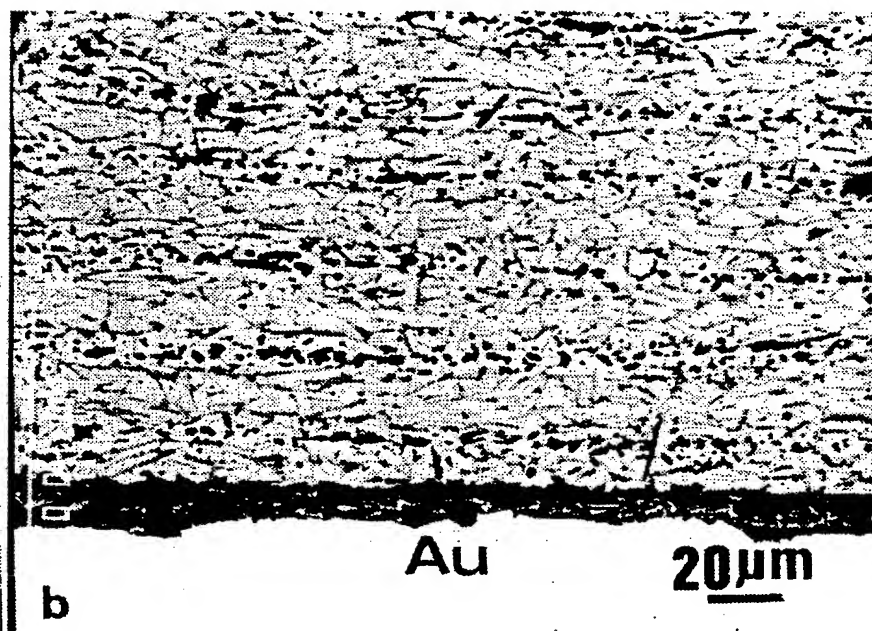
29. The method of claim 28 wherein the superconducting oxide is manufactured by a fabrication technique selected from a group consisting of powder processing of the individual metal oxides and pyrolysis of metal-organo precursors.

30. The method of claim 1 or 2 wherein the press coating technique is used to join superconductors and normal metals.

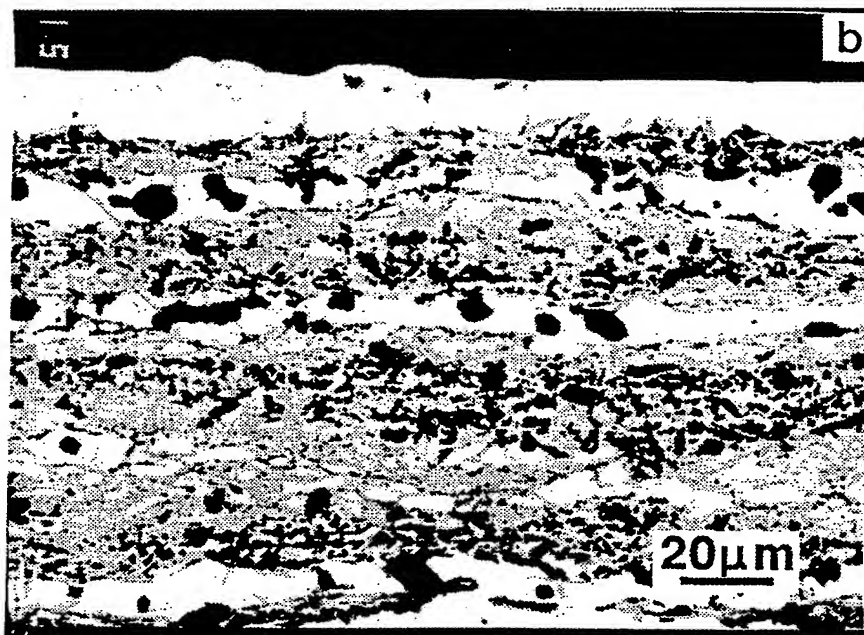
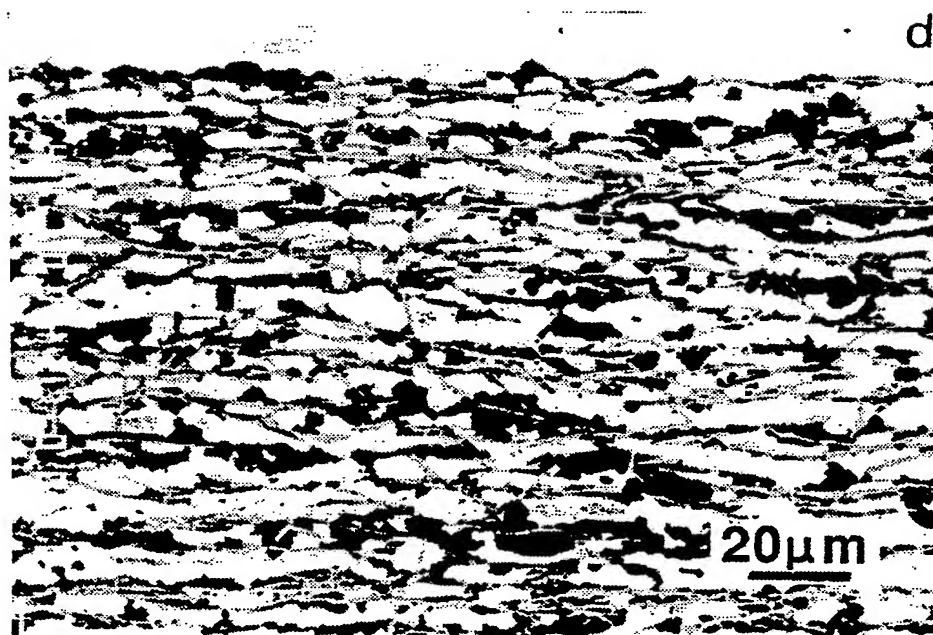
31. The method of claim 1 wherein said superconductor oxide is a superconductor oxide selected from the group consisting of Bi(Pb)-Sr-Ca-Cu-O, Yb-Ba-Cu-O, Y-Ba-Cu-O, and Tl-Ba-Ca-Cu-O.

32. An oxide superconductor composite prepared according to the methods described in claim 1 or 2.

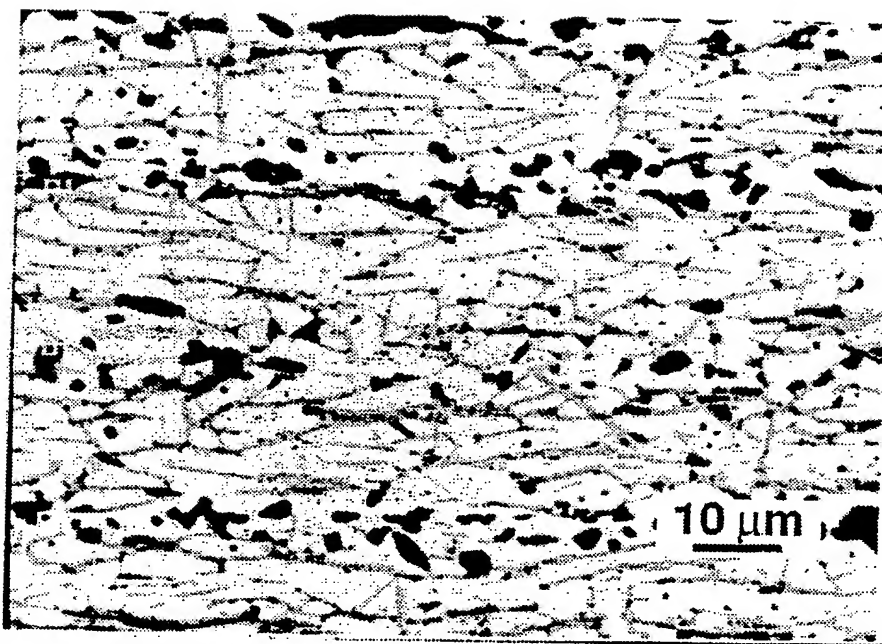
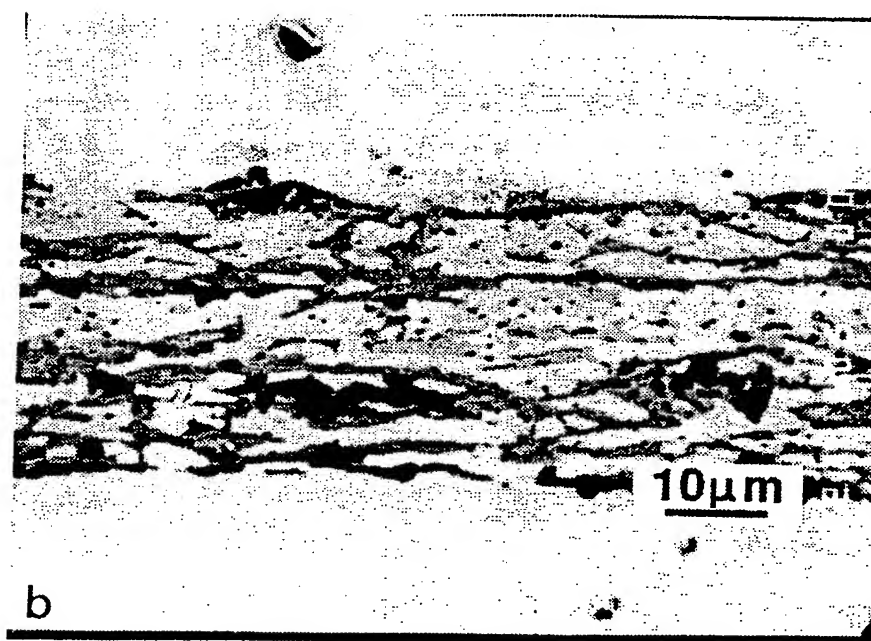
**FIG. 1****FIG. 2****SUBSTITUTE SHEET**

*FIG. 3**FIG. 4*

SUBSTITUTE SHEET

*FIG. 5**FIG. 6*

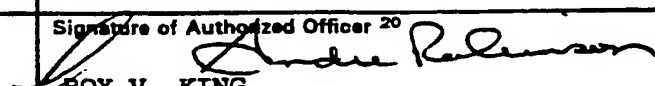
SUBSTITUTE SHEET

***FIG. 7******FIG. 8***

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01118

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5): B05D 5/12, 3/12 US CL : 505/1, 733, 734, 427/62, 356, 370, 428/469		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	505/1, 733, 734, 736, 427/62, 63, 356, 369, 370, 428/469, 156/303.1, 308.2	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category*	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US, A, 4,826,808, YUREK ET. AL., 02 MAY 1989 (SEE WHOLE DOCUMENT).	1-31
Y	US, A, 5,015,318, SMITS ET. AL., 14 MAY 1991 (SEE WHOLE DOCUMENT).	1-31
Y	J. APPL. PHYS. VOL. 66, NO. 1, ISSUED 01 JULY 1989, JIA ET. AL., 'SiO ₂ AND Si ₃ N ₄ PASSIVATION LAYERS ON Y-B _a -C _u -O THIN FILMS', (SEE PAGES 452-454).	27
Y	JPN. J. APPL. PHYS. VOL. 3, ISSUED MARCH 1990, NASU ET. AL., 'PREPARATION OF MOSTLY SINGLE HIGH-Tc PHASE THIN FILMS IN B ₁ , P _b -S _r -C _a -C _u -O BY PYROLYSIS OF ORGANIC ACID SALTS', (SEE PP. L450-452).	28-29
Y	J. MATER RES., VOL. 5, NO. 6, ISSUED JUNE 1990, SPANN ET. AL., 'ORIENTED BSCCO THICK FILM COATINGS ON POLYCRYSTALLINE MgO', (SEE PAGES 1163-1168).	32
<p>* Special categories of cited documents:¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of the International Search Report ²	
05 MAY 1992	07 MAY 1992	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 ROY V. KING	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)